Colouring preparations

The present invention relates to colorant preparations comprising

a) at least one colorant in particulate form,
b) at least one organic solvent having a boiling point of at least 247°C, measured at atmospheric pressure, and
c) water,

and less than 0.25% by weight of
organic solvents having a boiling point below 247°C, measured at atmospheric pressure.

Colorant preparations and especially inks which are used in the ink jet process (such as Thermal Ink Jet, Piezo Ink Jet, Continuous Ink Jet, Valve Jet, transfer printing processes) have to meet a whole series of requirements: They have to have viscosity and surface tension suitable for printing, they have to be stable in storage, i.e., they should not coagulate or flocculate, and they must not lead to cloggage of printer nozzles, which can be problematical especially in the case of inks comprising dispersed, i.e., undissolved, colorant particles. Stability in storage further requires of these inks that the dispersed colorant particles do not sediment. Furthermore, in the case of Continuous Ink Jet, the inks shall be stable to the addition of conducting salts and be free from any tendency to floc out with an increase in the ion content. In addition, the prints obtained have to meet colorists' requirements, i.e., show high brilliance and depth of shade, and have good fastnesses, for example rubfastness, lightfastness, waterfastness and wet rubfastness, if necessary after aftertreatment such as fixation for example, and good drying characteristics.

It is a further requirement that the inks dry rapidly on the substrate in order that images or characters to be printed do not bleed and for example the ink droplets of different colors do not mingle. The production of needle-sharp prints requires in this connection not only print dry time minimization but also bleed control for the ink droplets on the substrate during the print dry time. An ink where the droplets do not bleed is said to have good holdout. Prior art ink holdout or print definition leaves something to be desired.

US 5,141,556 discloses aqueous inks and their use in ink jet printing which comprise a dye or a dispersed pigment and also, as a component c), hexene-1,2-diol or an aliphatic 1,2-diol or 1,3-diol, with branched 1,2-diols being preferred. However, the inks still leave room for improvement.

EP 0 649 888 describes ink compositions for the ink jet printing process which, as well as water and a soluble dye, comprise propylene glycol mono-n-butyl ether and/or dipropylene glycol mono-n-butyl ether and also some other water-soluble butyl ether. The inks thus obtainable produce good images on recycled paper; however, ink droplet holdout on less absorbent materials is unsatisfactory.

EP-A 0 514 159 discloses aqueous inks which comprise soluble dyes and a selection of organic solvents. The inks described in EP-A 0 514 159 likewise leave room for improvement.

It is an object of the present invention to provide colorant preparations and especially inks for the ink jet process which do not have the disadvantages mentioned above. It is a further object of the present invention to provide a process for producing improved colorant preparations. It is a further object of the present invention to provide printed substrates.

We have found that the first object is achieved by the colorant preparations defined at the beginning.

The inventive colorant preparations comprise colorants in particulate form a), for example pigments or disperse dyes. Pigments for the purposes of the present invention are virtually insoluble, finely dispersed, organic or inorganic colorants as per the definition in German standard specification DIN 55944.

Representative examples of pigments are

- monoazopigments:	C.I. Pigment Brown 25; C.I. Pigment Orange 5, 13, 36 and 67; C.I. Pigment Red 1, 2, 3, 5, 8, 9, 12, 17, 22, 23, 31, 48:1, 48:2, 48:3, 48:4, 49, 49:1, 52:1, 52:2, 53, 53:1, 53:3, 57:1, 63, 112, 146, 170, 184, 210, 245 and 251; C.I. Pigment Yellow 1, 3, 73, 74, 65, 97, 151 and 183;
- disazo pigments:	C.I. Pigment Orange 16, 34 and 44; C.I. Pigment Red 144, 166, 214 and 242; C.I. Pigment Yellow 12, 13, 14, 16, 17, 81, 83, 106, 113, 126, 127, 155, 174, 176 and 188;
- anthanthrone pigments:	C.I. Pigment Red 168 (C.I. Vat Orange 3);
- anthraquinone pigments:	C.I. Pigment Yellow 147 and 177; C.I. Pigment Violet 31;

- anthraquinone pigments: C.I. Pigment Yellow 147 and 177; C.I. Pigment Violet 31;

- anthrapyrimidine pigments: C.I. Pigment Yellow 108 (C.I. Vat Yellow 20);

- quinacridone pigments: C.I. Pigment Red 122, 202 and 206; C.I. Pigment Violet 19;

- quinophthalone pigments: C.I. Pigment Yellow 138;

- dioxazine pigments: C.I. Pigment Violet 23 and 37;

- flavanthrone pigments: C.I. Pigment Yellow 24 (C.I. Vat Yellow 1);

- indanthrone pigments: C.I. Pigment Blue 60 (C.I. Vat Blue 4) and 64 (C.I. Vat Blue 6);

- isoindoline pigments: C.I. Pigment Orange 69; C.I. Pigment Red 260; C.I. Pigment Yellow 139 and 185;

- isoindolinone pigments: C.I. Pigment Orange 61; C.I. Pigment Red 257 and 260; C.I. Pigment Yellow 109, 110, 173 and 185;

- isoviolanthrone pigments: C.I. Pigment Violet 31 (C.I. Vat Violet 1);

- metal complex pigments: C.I. Pigment Yellow 117, 150 and 153; C.I. Pigment Green 8;

- perinone pigments: C.I. Pigment Orange 43 (C.I. Vat Orange 7); C.I. Pigment Red 194 (C.I. Vat Red 15);

- perylene pigments: C.I. Pigment Black 31 and 32; C.I. Pigment Red 123, 149, 178, 179 (C.I. Vat Red 23), 190 (C.I. Vat Red 29) and 224; C.I. Pigment Violet 29;

- phthalocyanine pigments: C.I. Pigment Blue 15, 15:1, 15:2, 15:3, 15:4, 15:6 and 16; C.I. Pigment Green 7 and 36;

- pyranthrone pigments: C.I. Pigment Orange 51; C.I. Pigment Red 216 (C.I. Vat Orange 4);

- thioindigo pigments: C.I. Pigment Red 88 and 181 (C.I. Vat Red 1); C.I. Pigment Violet 38 (C.I. Vat Violet 3);

- triarylcarbonium pigments: C.I. Pigment Blue 1, 61 and 62; C.I. Pigment Green 1; C.I. Pigment Red 81, 81:1 and 169; C.I. Pigment Violet 1, 2, 3 and 27; C.I. Pigment Black 1 (aniline black);

- C.I. Pigment Yellow 101 (aldazine yellow);

- C.I. Pigment Brown 22.

Examples of inorganic pigments are:

– white pigments: titanium dioxide (C.I. Pigment White 6), zinc white, pigment grade zinc oxide; zinc sulfide, lithopone; lead white;

– black pigments: iron oxide black (C.I. Pigment Black 11), iron manganese black, spinell black (C.I. Pigment Black 27); carbon black (C.I. Pigment Black 7);

– chromatic pigments: chromium oxide, chromium oxide hydrate green; chrome green (C.I. Pigment Green 48); cobalt green (C.I. Pigment Green 50); ultramarine green; cobalt blue (C.I. Pigment Blue 28 and 36); ultramarine blue; iron blue (C.I. Pigment Blue 27); manganese blue; ultramarine violet; cobalt violet, manganese violet; iron oxide red (C.I. Pigment Red 101); cadmium sulfoselenide (C.I. Pigment Red 108); molybdate red (C.I. Pigment Red 104); ultramarine red;

iron oxide brown, mixed brown, spinell and corundum phases (C.I. Pigment Brown 24, 29 and 31), chrome orange;

iron oxide yellow (C.I. Pigment Yellow 42); nickel titanium yellow (C.I. Pigment Yellow 53; C.I. Pigment Yellow 157 and 164); chrome titanium yellow; cadmium sulfide and cadmium zinc sulfide (C.I. Pigment Yellow 37 and 35); chrome yellow (C.I. Pigment Yellow 34), zinc yellow, alkaline earth metal chromates; Naples yellow, bismuth vanadate (C.I. Pigment Yellow 184);

- interference pigments: metallic effect pigments based on coated metal platelets; pearl luster pigments based on mica platelets coated with metal oxide, liquid crystal pigments.

Preferred pigments in this context are monoazo pigments (especially laked BONS pigments, naphthol AS pigments), disazo pigments (especially diaryl yellow pigments, bisacetoacetanilide pigments, disazopyrazolone pigments), quinacridone pigments, quinophthalone pigments, perinone pigments, phthalocyanine pigments, triarylcarbonium pigments (alkali blue pigments, laked rhodamines, dye salts with complex anions), isoindoline pigments and carbon blacks.

Specific examples of particularly preferred pigments are: C.I. Pigment Yellow 138, C.I. Pigment Red 122, C.I. Pigment Violet 19, C.I. Pigment Blue 15:3 and 15:4, C.I. Pigment Black 7, C.I. Pigment Orange 5, 38 and 43 and C.I. Pigment Green 7.

The pigments recited above are advantageously useful for preparing ink jet ink sets based on the inventive colorant preparations. The level of the particular pigments in the individual colorant preparations or inks must be adapted to the particular requirements (trichromatic coloration, for example), i.e., cyan, magenta, yellow and black pigments have to be coordinated with each other with regard to content.

The following pigment combinations are particularly commendable for trichromatic requirements:

- C.I. Pigment Yellow 138, C.I. Pigment Violet 19, C.I. Pigment Blue 15:3 and C.I. Pigment Black 7;

- C.I. Pigment Yellow 138, C.I. Pigment Red 122, C.I. Pigment Blue 15:3 or 15:4 and C.I. Pigment Black 7;

- C.I. Pigment Yellow 138, C.I. Pigment Violet 19, C.I. Pigment Blue 15:3, C.I. Pigment Black 7, C.I. Pigment Orange 43 and C.I. Pigment Green 7;

- C.I. Pigment Yellow 138, C.I. Pigment Red 122, C.I. Pigment Blue 15:3 or 15:4, C.I. Pigment Black 7, C.I. Pigment Orange 5 and C.I. Pigment Green 7;

- C.I. Pigment Yellow 138, C.I. Pigment Red 122, C.I. Pigment Blue 15:3 or 15:4, C.I. Pigment Black 7, C.I. Pigment Orange 38 and C.I. Pigment Green 7;

- C.I. Pigment Yellow 138, C.I. Pigment Red 122, C.I. Pigment Blue 15:3 or 15:4, C.I. Pigment Black 7, C.I. Pigment Orange 43 and C.I. Pigment Green 7.

Specific examples of representative disperse dyes are:

- C.I. Disperse Yellow 2, 4, 5, 6, 7, 8, 10, 11, 11:1, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 40, 41, 42, 43, 44, 45, 46, 47, 48, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 179, 180, 181, 182, 183, 184, 184:1, 198, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227 and 228;

- C.I. Disperse Orange 2, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 25:1, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 38, 39, 40, 41, 41:1, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 126, 127, 128, 129, 130, 131, 136, 137, 138, 139, 140, 141, 142, 143, 145, 146, 147 and 148;

- C.I. Disperse Red 2, 3, 4, 5, 5:1, 6, 7, 8, 9, 10, 12, 13, 14, 15, 16, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 30:1, 31, 32, 33, 34, 35, 36, 38, 39, 40, 41, 43, 43:1, 46, 48, 50, 51, 52, 53, 54, 55, 55:1, 56, 58, 59, 60, 61, 63, 65, 66, 69, 70, 72, 73, 74, 75, 76, 77, 79, 80, 81, 82, 84, 85, 86, 86:1, 87, 88, 89, 90, 91, 92, 93, 94, 96, 97, 98, 100, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 115, 116, 117, 118, 120, 121, 122, 123, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 151:1, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 167:1, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 190:1, 191, 191:1, 192, 193, 194, 195, 211, 223, 224, 273, 274, 275, 276, 277, 278, 279, 280, 281, 302:1, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 338, 339, 340, 341, 342, 343, 344, 346, 347, 348, 349, 352, 356 and 367;

- C.I. Disperse Violet 1, 2, 3, 4, 4:1, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 31, 33, 34, 35, 36, 37, 38, 39, 40, 41,

42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 70, 81, 86, 87, 88, 89, 91, 92, 93, 94, 96 and 97;

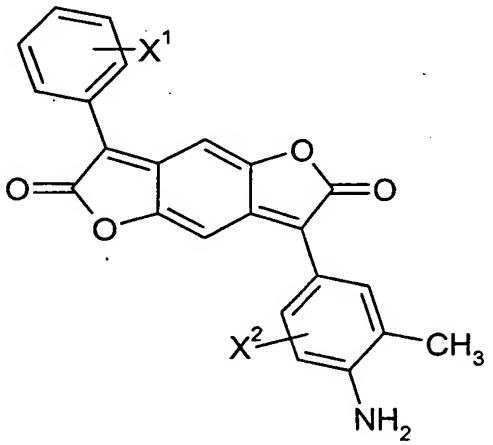
- C.I. Disperse Blue 2, 4, 5, 6, 8, 9, 10, 11, 12, 13, 13:1, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 23:1, 24, 25, 27, 28, 29, 30, 31, 32, 33, 34, 36, 38, 39, 40, 42, 43, 44, 45, 47, 48, 49, 51, 52, 53, 54, 55, 56, 58, 60, 60:1, 61, 62, 63, 64, 64:1, 65, 66, 68, 70, 72, 73, 75, 76, 77, 79, 80, 81, 81:1, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 103, 104, 105, 107, 108, 109, 111, 112, 113, 114, 115, 116, 117, 118, 119, 121, 122, 123, 125, 126, 127, 128, 130, 131, 132, 133, 134, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 158, 159, 160, 161, 162, 163, 164, 165, 165:2, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 195, 281, 282, 283, 283:1, 284, 285, 286, 287, 288, 289, 290, 291, 292, 293, 294, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 349, 351 and 359;

- C.I. Disperse Green 1, 2, 5, 6 and 9;

- C.I. Disperse Brown 1, 2, 3, 4, 4:1, 5, 7, 8, 9, 10, 11, 18, 19, 20 and 21;

- C.I. Disperse Black 1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 20, 22, 24, 25, 26, 27, 28, 29, 29:1, 30, 31, 32, 33, 34 and 36;

Also suitable are the substituted benzodifuranone dyes whose basic structure conforms to the formula A.

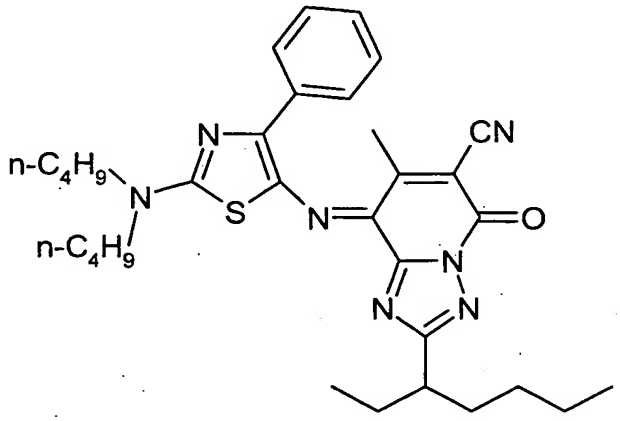


A

Such dyes may be substituted on either or both of the phenyl rings. Useful substituents X^1 and X^2 include halogen, alkyl with or without interruption by nonadjacent oxygen

atoms, alkoxy with or without interruption by oxygen atoms and substitution in the alkyl moiety, hydroxyl, substituted or unsubstituted amino, cyano, nitro and alkoxycarbonyl.

Also suitable is the dye of the following formula B:



B

Further examples of disperse dyes are recited in WO 97/46623, WO 98/24850 and WO 99/29783.

The inventive colorant preparations may comprise mixtures of two or more different colorants. Preferably, however, inventive colorant preparations do not comprise mixtures of two or more different colorants, but only one colorant.

The inventive colorant preparations comprise colorants which are in particulate form, i.e., in the form of particles. The particles may be regular or irregular in shape in that, for example, the particles may have a spherical or substantially spherical shape or a needle (acicular) shape.

In one embodiment of the present invention, the particles are present in spherical or substantially spherical form, i.e., the ratio of the longest diameter to the smallest diameter is in the range from 1.0 to 2.0 and preferably up to 1.5.

Colorants in particulate form which are comprised in the inventive colorant preparations should be very finely divided. It is preferable for 95% by weight and more preferable for 99% by weight of the colorant particles to have a median particle diameter of 1 µm, preferably of 0.5 µm and especially of 0.2 µm.

In a preferred embodiment of the present invention, an inventive colorant preparation comprises from 10 to 100 g/l and preferably from 12 to 70 g/l of colorant in particulate form.

Component b) of inventive colorant preparations and especially inventive inks for the ink jet process is at least one organic solvent having a boiling point of at least 247°C and preferably of at least 250°C, measured at atmospheric pressure.

Preferably, organic solvents b) comprised in the inventive colorant preparations are characterized in that their decomposition point is at least 200°C or higher.

Low molecular weight polytetrahydrofuran is a preferred organic solvent b), it can be used alone or preferably in admixture with one or more high-boiling water-soluble or water-miscible organic solvents.

The low molecular weight polytetrahydrofuran whose use is preferable customarily has an average molecular weight M_w in the range from 150 to 500 g/mol, preferably in the range from 200 to 300 g/mol and more preferably of about 250 g/mol (corresponding to a molecular weight distribution).

Polytetrahydrofuran is preparable in a conventional manner by cationic polymerization of tetrahydrofuran. This produces linear polytetramethylene glycols.

When polytetrahydrofuran is used in admixture with further organic solvents, the organic solvents used are generally high-boiling (i.e., the boiling point is generally ≥ 247°C at atmospheric pressure) and are soluble in or miscible with water.

Useful solvents include polyhydric alcohols, preferably unbranched and branched polyhydric alcohols having from 3 to 8 and especially from 3 to 6 carbon atoms, an example being glycerol.

Useful solvents further include polyethylene glycols and polypropylene glycols, which terms also comprehend the lower polymers (tri- and tetramers). Preference is given to polyethylene glycols and polypropylene glycols having average molecular weights M_n in the range from 120 to 1500 g/mol, especially in the range from 200 to 800 g/mol and particularly in the range from 300 to 500 g/mol. Specific examples are triethylene glycol, tetraethylene glycol, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, triethylene glycol monopropyl ether, triethylene glycol monobutyl ether, tri- and tetra-1,2- and -1,3-propylene glycol and tri- and tetra-1,2- and -1,3-propylene glycol monomethyl, monoethyl, monopropyl and monobutyl ethers.

Examples of particularly preferred solvents are glycerol, polyethylene glycol (M_n 300-500 g/mol), diethylene glycol monobutyl ether and triethylene glycol monobutyl ether.

Polytetrahydrofuran may also be mixed with one or more (e.g., two, three or four) of the solvents recited above.

In one embodiment of the present invention, inventive colorant preparations and especially inventive inks for the ink jet process may comprise from 0.1% to 45% by weight, preferably from 5% to 30% by weight, more preferably from 10% to 25% by weight and most preferably from 10% to 20% by weight of organic solvents.

Organic solvents for the purposes of the present invention are liquid at room temperature.

Inventive colorant preparations and especially inventive inks for the ink jet process comprise no organic solvents which have a boiling point below 247°C, measured at atmospheric pressure. By "no solvents" as used herein is meant that the fraction of organic solvents having a boiling point below 247°C that may be present as an impurity or as a contaminant is in total less than 0.25% by weight, preferably less than 0.1% by weight and more preferably less than 0.05% by weight, the amounts in % by weight being in each case based on the inventive colorant preparation.

Examples of organic solvents having a boiling point below 247°C are for example ethylene glycol, diethylene glycol, N-methylpyrrolidone, propylene glycol, propylene carbonate, diethylene monomethyl ether, diethylene monethyl ether, diethylene mono-n-butyl ether, di-n-butyl ether, 1,2-dimethoxyethane, isopropanol and ethanol.

The organic solvents, including especially the particularly preferred solvent combinations mentioned, may advantageously be supplemented with urea (preferably from 0.1% to 5% by weight, based on the weight of the inventive colorant preparation or of the inventive ink for the ink jet process) to further enhance the water-retaining effect of the solvent mixture.

The inventive colorant preparations and especially the inventive inks for the ink jet process may comprise further assistants of the kind which are customary especially for aqueous ink jet inks and in the printing and coatings industry. Examples of such assistants include erythritol, pentaerythritol, pentitols such as arabitol, adonitol and xylitol and hexitols such as sorbitol, mannitol and dulcitol. Further examples are polyethylene glycols having an M_w in the range from more than 2000 g/mol to about

10 000 g/mol and preferably up to 800 g/mol. Further examples are preservatives such as for example 1,2-benzisothiazolin-3-one and its alkali metal salts, degasers/defoamers such as for example ethoxylated acetylenediols, which customarily comprise from 20 to 40 mol of ethylene oxide per mole of acetylenediol and may also have a dispersing effect, viscosity regulators, flow agents, wetters (e.g., wetting surfactants based on ethoxylated or propoxylated fatty or oxo alcohols, propylene oxide-ethylene oxide block copolymers, ethoxylates of oleic acid or alkylphenols, alkylphenol ether sulfates, alkylpolyglycosides, alkyl phosphonates, alkylphenyl phosphonates, alkyl phosphates, alkylphenyl phosphates or preferably polyethersiloxane copolymers, especially alkoxylated 2-(3-hydroxypropyl)heptamethyl-trisiloxanes, which generally comprise a block of from 7 to 20 and preferably from 7 to 12 ethylene oxide units and a block of from 2 to 20 and preferably from 2 to 10 propylene oxide units and may be comprised in the colorant preparations in amounts from 0.05% to 1% by weight), anti-settlers, luster improvers, lubricants, adhesion improvers, anti-skinning agents, delusterants, emulsifiers, stabilizers, hydrophobicizers, light control additives, hand improvers, antistats, bases such as for example K_2CO_3 or acids, specifically carboxylic acids such as for example lactic acid or citric acid for regulating the pH. When these agents are part of the inventive colorant preparations and especially inventive inks for the ink jet process, their total amount is generally 2% by weight and especially 1% by weight, based on the weight of the inventive colorant preparations and especially of the inventive inks for the ink jet process.

The inventive colorant preparations may further comprise dispersants. Examples of useful dispersants include alkoxylated and partially sulfated alkylphenols, such as the substances described in US 4,218,218, condensation products of naphthalenesulfonic acid and formaldehyde or mixtures of arylsulfonic acid-formaldehyde condensation products as described for example in US 5,186,846.

Useful dispersants further include ethoxylated fatty alcohols of the formula

$$C_xH_{2x+1}O(CH_2CH_2O)_yH,$$

where x is an integer in the range from 12 to 30 and preferably up to 18 and y is an integer in the range from 3 to 50.

Useful dispersants further include maleic acid-acrylic acid copolymers, especially those having a molecular weight M_n in the range from 2000 to 10 000 g/mol, which are useful in the form of random copolymers or block copolymers. Useful dispersants further include N-vinylpyrrolidone homopolymers and acrylate-N-vinylpyrrolidine copolymers, especially those N-vinylpyrrolidone homopolymers and acrylate-N-vinylpyrrolidine

copolymers having a molecular weight M_n in the range from 2000 to 10 000 g/mol, in the form of random copolymers or block copolymers.

In one embodiment of the present invention, inventive colorant preparations and especially inventive inks for the ink jet process comprise binders. Binders can be selected from the group of the radiation-curable binders, the thermally curable binders and the air-drying binders. Useful binders are described for example in WO 99/01516 and WO 02/36695. Similarly, dispersing binder systems as in WO 03/29318 are useful as an additive.

In one embodiment of the present invention, inventive colorant preparations and especially inventive inks for the ink jet process have a dynamic viscosity in the range from 1 to 30 mPa·s, preferably in the range from 1 to 20 mPa·s and more preferably in the range from 2 to 15 mPa·s, determined at 20°C in each case.

The surface tension of inventive colorant preparations and especially inventive inks for the ink jet process at 20°C is generally in the range from 20 to 70 mN/m, especially in the range from 20 to 40 mN/m and more preferably in the range from 25 to 35 mN/m.

The pH of inventive colorant preparations and especially inventive inks for the ink jet process is generally in the range from 5 to 10 and preferably in the range from 7 to 9.

Component c) of the inventive colorant preparations is water, preferably deionized water. The preferred water content is at least 30% by weight, preferably at least 45% by weight and more preferably at least 65% by weight.

In one embodiment of the present invention, inventive colorant preparations and especially inventive inks for the ink jet process comprise less than 500 ppm of free heavy metal ions, preferably less than 400 ppm, based in each case on the mass of the inventive colorant preparation or of the inventive ink for the ink jet process. Specific examples of heavy metal ions are: Cu^{2+}, Co^{2+}, Co^{3+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Ca^{2+}. More particularly, inventive colorant preparations and inventive inks for the ink jet process comprise up to 300 ppm of iron.

Inventive colorant preparations and especially inventive inks for the ink jet process having less than 500 ppm of heavy metal ions are producible for example by using purified pigments or by employing steps such as precipitating, salting out, ion exchange processes, filtration, electrolytic processes or other conventional deionization processes during the production of the inventive colorant preparations and especially of

the inventive inks for the ink jet process. It is also possible to use correspondingly purified organic solvent and completely ion-free water.

In one embodiment of the present invention, inventive colorant preparations and especially inventive inks for the ink jet process comprise less than 0.05% by weight of chloride, determined as sodium chloride.

Inventive colorant preparations and especially inventive inks are generally friendly to the environment.

A further aspect of the present invention is a process for producing inventive colorant preparations, hereinafter also referred to as inventive production process. The inventive production process customarily comprises one or more steps in which various components are mixed. Such steps are carried out in customary mixing apparatuses, for example dissolvers, tanks and mills, including ball mills, including stirred ball mills.

In one embodiment of the inventive production process, colorant in particulate form (a), for example in the form of an aqueous press cake, is premixed together with at least one organic solvent (b), water (c) in a suitable apparatus, for example a dissolver. The resulting mixture is subsequently ground in a mill to achieve the desired particle size (generally a maximum diameter of 1 µm, especially 0.5 µm, and more preferably 0.2 µm).

Inventive colorant preparations can be used directly as or for producing inks. More particularly, inventive colorant preparations can be used directly as or for producing inks for the ink jet process. Other suitable inks are fountain pen inks for example.

To produce inks from inventive colorant preparations, one embodiment of the present invention comprises as sufficient steps setting the desired colorant concentration by addition of further water to the inventive colorant preparations, if appropriate adding further additives and finally filtering using a filtering means with fines removal in the range from 1 to 0.5 µm. Inventive ink jet inks can be obtained in this way.

A further aspect of the present invention is a process for printing substrates, which can be sheetlike or three dimensional for example, by the ink jet process using inventive colorant preparations or inventive inks. To this end, inventive colorant preparations or inventive ink jet inks are printed onto the substrate and the print obtained is then optionally fixed.

In the ink jet process, the typically aqueous inks are sprayed as small droplets directly onto the substrate. There is a continuous form of the process, in which the ink is pressed at a uniform rate through a nozzle and the jet is directed onto the substrate by an electric field depending on the pattern to be printed, and there is an interrupted or drop-on-demand process, in which the ink is expelled only where a colored dot is to appear, the latter form of the process employing either a piezoelectric crystal or a heated hollow needle (bubble or thermal jet process) to exert pressure on the ink system and so eject an ink droplet. These techniques are described in Text. Chem. Color 19 (1987), No. 8, 23-29, and 21 (1989), No. 6, 27-32.

The inks of the invention are particularly useful as inks for the bubble jet process or the process employing a piezoelectric crystal.

Useful substrate materials include:

cellulosic materials such as paper, paperboard, cardboard, wood and woodbase, which may each be lacquered or otherwise coated,

metallic materials such as foils, sheets or workpieces composed of aluminum, iron, copper, silver, gold, zinc or alloys thereof, which may each be lacquered or otherwise coated,

silicatic materials such as glass, porcelain and ceramic, which may likewise each be coated,

polymeric materials of any kind such as polystyrene, polyamides, polyesters, polyethylene, polypropylene, melamine resins, polyacrylates, polyacrylonitrile, polyurethanes, polycarbonates, polyvinyl chloride, polyvinyl alcohols, polyvinyl acetates, polyvinylpyrrolidones and corresponding copolymers including block copolymers, biodegradable polymers and natural polymers such as gelatin,

leather - both natural and artificial - in the form of smooth leather, nappa leather or suede leather,

comestibles and cosmetics,

and in particular

textile substrates and sheetlike structures such as wovens, knit fabric, woven fabric, nonwovens and made-up fabric composed for example of polyester, modified

polyester, blend fabrics from more than two materials such as polyester blend wovens and cotton blend wovens, cellulosic materials such as cotton, jute, flax, hemp and ramie, viscose, wool, silk, polyamide, polyamide blend wovens, polyacrylonitrile, polyurethane, polytetrahydrofuran, triacetate, acetate, polycarbonate, polypropylene, polyvinyl chloride, polyester microfibers and glass fiber wovens.

Inventive colorant preparations and especially inventive inks for the ink jet process have altogether advantageous performance properties, especially good start-of-print performance and good sustained use performance (kogation) and also good holdout, and produce printed images of high quality, i.e., of high brilliance and depth of shade and also high rub-, light-, water- and wet rubfastness, washfastness and also stability to chemical dry cleaning. They are particularly useful for printing coated and plain paper and also textile substrates.

A further embodiment of the present invention provides substrates, especially textile substrates, which have been printed by one of the abovementioned inventive processes and are notable for particularly crisply printed pictures or drawings and also excellent hand.

In a further embodiment of the present invention, at least two and preferably at least three different inventive inks for the ink jet process can be combined into sets.

A working example illustrates the invention.

Example 1

1a) Dispersing a pigment

The following were ground together in a Drais DCP SF 12 Superflow stirred ball mill:

1800 g	of	Pigment Blue 15:3
450 g	of	n-$C_{18}H_{37}O(CH_2CH_2O)_{25}H$
3700 g	of	distilled water

Grinding was continued until the pigment particles had a mean diameter of 100 nm.

1b) Production of an inventive colorant preparation

The following were mixed in a glass beaker:

17 g	of	the dispersed pigment from 1a)

15 g of glycerol (boiling point: 290°C)
1 g of polyethylene glycol (M_n 8000 g/mol)
7 g of polyethylene glycol (M_n 400 g/mol)
5 g of polytetrahydrofuran (M_n 250 g/mol)
0.2 g of Tego Wet® 250, a wetting agent having a boiling point >>250°C
1 g of urea
53.8 g of completely ion-free water

The colorant preparation obtained was subsequently filtered through a sieve having a pore diameter of 1 µm.

The glycerol, polyethylene glycols and polytetrahydrofuran used had a free heavy metal ion content of below 500 ppm, based respectively on glycerol used, polyethylene glycols used and polytetrahydrofuran used.

The inventive colorant preparation was usable as an ink for the ink jet process. Very good results were achieved on printing substrates such as textile (cotton) for example.

Droplet holdout on substrates, in particular textile such as cotton, was very good.